To Bjorn Bartels, PhD
Scientist and Human
Who will be missed

Aromaticity

Ramil Baiazitov

October 29, 2002
Outline

1. History of aromaticity and different kinds of it
2. Criteria of aromaticity and antiaromaticity
   - Energetic criteria
   - Structural criteria
   - Chemical criteria
   - Magnetic criteria (ring current)
     - NMR chemical shift
     - Magnetic susceptibility exaltation and anisotropy
3. Kinds of aromaticity (anti-, homo-, schizo-).
What was aromaticity?

<1825 – distinctive “aromatic” smell
<1865 – high C:H ratio, still stable
1865 – benzene structure (Kekule)
1866 – substitution is more favorable than addition (Erlenmeyer)
1910 – exalted diamagnetic susceptibility (Pascal)
1925 – electron sextet and heteroaromaticity (Armit-Robinson)
1931 – theory of cyclic \((4n+2)\pi\) systems (Huckel)
1936 – ring current theory (Pauling)
1937 – London diamagnetism
1956 – ring current effects on NMR shifts (Pople)

Summary of the definitions

1. Chemical behavior – reversion to type
2. Structural – bond length equalization due to delocalization
3. Energetic – enhanced stability
4. Magnetic – ring current effects
   - anomalous chemical shifts
   - large magnetic anisotropies
   - diamagnetic susceptibility exaltation

Hückel rule

\[ E_J = \alpha + 2\beta \cos(2\pi J/N) \]

\[ E_{\text{loc}} = 6(\alpha + \beta) \text{ or } 3(\alpha + 2.0699\beta) + 3(\alpha + 0.4660\beta) = 6\alpha + 7.61\beta \]

\[ E_n = 6\alpha + 8\beta \quad \Delta E = E_n - E_{\text{loc}} = 0.39\beta \]

\[ E_{\text{loc}} = 2(\alpha + 2.0699\beta) + 2(\alpha + 0.4660\beta) = 4\alpha + 5.07\beta \]

\[ E_n = 4\alpha + 4\beta \quad \Delta E = E_n - E_{\text{loc}} = -1.07\beta \]

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**Table I. Calculated Hückel \(\pi\)-Bond Energies of Carbon–Carbon Double Bonds and Carbon–Carbon Single Bonds of Acyclic Polyenes**

<table>
<thead>
<tr>
<th>Designation(^a)</th>
<th>Type of bond</th>
<th>Calculated (\pi)-bond energy, (\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>H(_2)C=CH</td>
<td>2.0000(^b)</td>
</tr>
<tr>
<td>22</td>
<td>H(_2)C=CH</td>
<td>2.0699</td>
</tr>
<tr>
<td>22'</td>
<td>H(_2)C=C</td>
<td>2.0000(^b)</td>
</tr>
<tr>
<td>21</td>
<td>H(_2)C=CH</td>
<td>2.1083</td>
</tr>
<tr>
<td>20</td>
<td>C=CH</td>
<td>2.1716</td>
</tr>
<tr>
<td>12</td>
<td>H(_2)C=CH</td>
<td>0.4660</td>
</tr>
<tr>
<td>11</td>
<td>H(_2)C=CH</td>
<td>0.4362</td>
</tr>
<tr>
<td>10</td>
<td>C=CH</td>
<td>0.4358</td>
</tr>
</tbody>
</table>

\(^a\) The first index gives the bond order, the second the number of attached hydrogens. \(^b\) Arbitrarily assigned.

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B.A. Hess, Jr., and L. J. Schaad, *JACS*, 1971, 93, 305
Criteria of aromaticity. Energetic criteria

\[ RE=\Delta H^o_a(PhH)-6E(C-H)-3E(C-C)-3E(C=C) \]

Hydrogenation:

\[ \text{\chem{I}} + H_2 \rightarrow \text{\chem{I}} \Delta H=-28.3 \text{kcal/mol} \]

\[ \text{\chem{C}} + 2H_2 \rightarrow \text{\chem{C}} \Delta H=-54.8 \text{ kcal/mol}(-28.3 \times 2 \pm 1.8) \]

\[ \text{\chem{C}} + 3H_2 \rightarrow \text{\chem{C}} \Delta H=-49.1 \text{kcal/mol}(-28.3 \times 3 \pm 35.8) \]

\[ \Delta H=35.8 \text{kcal/mol}=5.97 \text{kcal/}\pi\text{-electron}=RE \]

Isodesmic: \[ \text{\chem{C}} + 6\text{CH}_4 \rightarrow 3\text{C}_2\text{H}_6 \rightarrow 3\text{C}_2\text{H}_4 \]
\[ \Delta H=64.2 \text{kcal/mol} \]

Homodesmotic: \[ \text{\chem{C}} + 3\text{C}_2\text{H}_4 \rightarrow 3\text{trans-butadiene} \]
\[ \Delta H=21.6 \text{kcal/mol} \]

Hyper-Homodesmotic: \[ \text{\chem{C}} + 3\text{CH}_2=\text{CH-CH=CH}_2 \rightarrow 3\text{CH}_2=\text{CH-CH=CH-CH=CH}_2 \]
\[ \Delta H=23.4 \text{kcal/mol}(\text{calc}) \]

Criteria of aromaticity. Energetic criteria

\[ 4 \text{CH}_4 \rightarrow 2 \text{CH}_2=\text{CH}_2 + 2 \text{CH}_3-\text{CH}_3 \quad \Delta H = -70 \text{kcal/mol} \]

\[ 4 \text{CH}_4 \rightarrow \text{CH}_2=\text{CH}_2 + 3 \text{CH}_3-\text{CH}_3 \quad \Delta H = -28 \text{kcal/mol} - \text{strain energy} \]

\[ \Delta \Delta H = 52 \text{kcal/mol} - \text{aromatic destabilization energy} \]

\[ \text{[Diagram]} \quad +4 \text{H}_2 \rightarrow \text{[Ring]} \quad \Delta H = -100 \text{kcal/mol} \]

\[ + \text{H}_2 \rightarrow \text{[Ring]} \quad \Delta H = -23 \text{kcal/mol} \Rightarrow \Delta \Delta H = 4 \times 23 - 100 = 8 \text{kcal/mol} \]

\[ 4 \text{CH}_3\text{F} = 3 \text{CH}_4 + \text{CF}_4 \quad \Delta H = -35.8 \text{kcal/mol} \]
Criteria of aromaticity. Structural criteria.

π-delocalization => planar geometry + bond length equalization, cyclic

1.397 Å

1.565 Å vs. 1.344/1.355 Å

[n]-para-cyclophanes

n=5 φ = 23.7
n=6 φ = 18.6
n=7 φ = 14.2
n=8 φ = 8.4

bond alteration 0.025 Å

From V.I. Minkin et.al. *Aromaticity and Antiaromaticity* ..., Wiley: New York; 1994
Criteria of aromaticity. Chemical criteria.
Criteria of aromaticity. Magnetic criteria.

A. Magnetic Susceptibility Exaltation and Anisotropy

\[ \Delta \chi = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) \] - anisotropy of magnetic susceptibility

\[ \chi = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}) \] - mean molar magnetic susceptibility (isotropic media)

\[ \Lambda = \chi - (\Sigma \chi A + n\lambda C = C) = \chi - \chi_{calc} \]

\[ \chi_{anis} = 0.0 \]
\[ \Lambda = -51.1 \]

Criteria of aromaticity. Magnetic criteria.

A. Magnetic Susceptibility Exaltation and Anisotropy

\[ M = \chi B \]

\[ \Delta \chi = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) - \text{anisotropy of magnetic susceptibility} \]

\[ \chi = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}) - \text{mean molar magnetic susceptibility (isotropic media)} \]

\[ \Lambda = \chi - (\Sigma \chi A + n\lambda C = C) = \chi - \chi_{\text{calc}} \]

\[ \chi_{\text{anis}} \quad 0.0 \]
\[ \Lambda \quad -51.1 \]

Criteria of aromaticity. Magnetic criteria.

A. Magnetic Susceptibility Exaltation and Anisotropy

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>X</th>
<th>λ</th>
<th>Xexp/Xcalc</th>
</tr>
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<tbody>
<tr>
<td>CH2</td>
<td>11.36</td>
<td>S</td>
<td>16.9</td>
<td>C=C</td>
</tr>
<tr>
<td>H</td>
<td>2</td>
<td>N</td>
<td>9</td>
<td>CH3</td>
</tr>
<tr>
<td>C</td>
<td>7.36</td>
<td>Cl</td>
<td>18.5</td>
<td>C=C-C=C</td>
</tr>
<tr>
<td>O(alc)</td>
<td>5.3</td>
<td>Br</td>
<td>27.8</td>
<td>C≡C</td>
</tr>
<tr>
<td>O(ald/ket)</td>
<td>6.4</td>
<td>I</td>
<td>42.2</td>
<td>N=N</td>
</tr>
<tr>
<td>CO2(acids)</td>
<td>15.15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{align*}
6C2^*-H &= 6(3.2) = 19.2 \\
2C2-H &= 2(3.8) = 7.6 \\
2C-C* &= 2(2.6) = 5.2 \\
5C*-C* &= 5(2.4) = 12.0 \\
3C=C &= 3(2.2) = 6.6 \\
7xinner e-core &= 7(0.15) = 1.05
\end{align*}

X_{calc} = 51.65 \\
\Lambda = 59.8 - 51.65 = 8.1

Calculated anisotropies

<table>
<thead>
<tr>
<th>Aromatics</th>
<th>X_{anis}</th>
<th>λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>-62.9</td>
<td>-13.4</td>
</tr>
<tr>
<td>C\textsubscript{5}H\textsubscript{5}\textsuperscript{-}</td>
<td>-67.7</td>
<td>-17.2</td>
</tr>
<tr>
<td>napthale</td>
<td>-130.3</td>
<td>-28.2</td>
</tr>
<tr>
<td>pyrrole</td>
<td>-48.1</td>
<td>-12.1</td>
</tr>
<tr>
<td>azulene</td>
<td>-144</td>
<td>-42.9</td>
</tr>
<tr>
<td>C\textsubscript{4}H\textsubscript{4}</td>
<td>28.7</td>
<td>18</td>
</tr>
<tr>
<td>C\textsubscript{5}H\textsubscript{5}\textsuperscript{+}</td>
<td>58.1</td>
<td>32.6</td>
</tr>
<tr>
<td>C\textsubscript{8}H\textsubscript{8}</td>
<td>146.3</td>
<td>60.4</td>
</tr>
<tr>
<td>pentalene</td>
<td>12.8</td>
<td>30.9</td>
</tr>
<tr>
<td>heptalene</td>
<td>168.3</td>
<td>76.7</td>
</tr>
</tbody>
</table>

Hyp J. Dauben, Jr., James D. Wilson, and John L. Laity JACS, 1968, 90, 811
Criteria of aromaticity. Magnetic criteria.

### Table I. Diamagnetic Exaltation Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \chi_M )</th>
<th>( \chi_M' )</th>
<th>( \Lambda )</th>
<th>Compound</th>
<th>( \chi_M )</th>
<th>( \chi_M' )</th>
<th>( \Lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nonaromatic Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>Benzenoid Aromatic Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>59.2 *</td>
<td>56.8</td>
<td>2.4</td>
<td>Phenanthrene</td>
<td>127.9 *</td>
<td>81.7</td>
<td>48.6</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>49.5 ± 0.5 *</td>
<td>47.0</td>
<td>2.5</td>
<td>Tetracene (4)</td>
<td>168 *</td>
<td>102</td>
<td>66</td>
</tr>
<tr>
<td>Cyclopentadiene (1)</td>
<td>44.5 ± *</td>
<td>38.0</td>
<td>6.5</td>
<td>Chrysene (5)</td>
<td>167.5 *</td>
<td>102</td>
<td>65</td>
</tr>
<tr>
<td>5,5-Dimethylcyclopentadiene (2)</td>
<td>67.5 ± 0.6 *</td>
<td>62.7</td>
<td>4.8</td>
<td>Pentacene (6)</td>
<td>205 *</td>
<td>122</td>
<td>83</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>68.1 *</td>
<td>68.1</td>
<td>0.0</td>
<td>Dibenz[a,h]anthracene (7)</td>
<td>193 *</td>
<td>122</td>
<td>71</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>57.5 *</td>
<td>58.3</td>
<td>-0.8</td>
<td>Fluoranthene (8)</td>
<td>138 *</td>
<td>96</td>
<td>42</td>
</tr>
<tr>
<td>1,3-Cyclohexadiene</td>
<td>48.6 *</td>
<td>49.3</td>
<td>-0.7</td>
<td>Pyrene (9)</td>
<td>155</td>
<td>98</td>
<td>57</td>
</tr>
<tr>
<td>1,4-Cyclohexadiene</td>
<td>48.7 *</td>
<td>48.5</td>
<td>0.2</td>
<td>Triphenylene (10)</td>
<td>157</td>
<td>107</td>
<td>70</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>78.9 ± 0.7 *</td>
<td>79.5</td>
<td>-0.6</td>
<td>Perylene (11)</td>
<td>171 *</td>
<td>121</td>
<td>50</td>
</tr>
<tr>
<td>Cycloheptene</td>
<td>69.3 ± 0.6 *</td>
<td>69.7</td>
<td>-0.4</td>
<td>Benzo[a]pyrene (12)</td>
<td>194 *</td>
<td>119</td>
<td>75</td>
</tr>
<tr>
<td>1,3-Cycloheptadiene</td>
<td>61.0 ± 0.6 *</td>
<td>60.7</td>
<td>0.3</td>
<td>Coronene (13)</td>
<td>243 *</td>
<td>140</td>
<td>103</td>
</tr>
<tr>
<td>1,4-Cycloheptadiene</td>
<td>61.0 ± 0.4 *</td>
<td>59.9</td>
<td>1.1</td>
<td>Ovalene (14)</td>
<td>354 *</td>
<td>181</td>
<td>173</td>
</tr>
<tr>
<td>1,3,5-Cycloheptatriene</td>
<td>59.8 ± 1.0 *</td>
<td>51.7</td>
<td>8.1</td>
<td><strong>Nonbenzenoid Aromatic and Pseudoaromatic Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,7,7-Trimethyl-1,3,5-cycloheptatriene</td>
<td>95.6 ± 0.4 *</td>
<td>88.5</td>
<td>7.1</td>
<td>Azulene (15)</td>
<td>91.0 *</td>
<td>61.4</td>
<td>29.6</td>
</tr>
<tr>
<td>7,7-Bis(cycloheptatrienyl)</td>
<td>119 ± 3 *</td>
<td>100.0</td>
<td>19.0</td>
<td>1,6-Methano[10] annulene (16)</td>
<td>119.9 ± 0.4 *</td>
<td>75.1</td>
<td>36.8</td>
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<tr>
<td>Cyclooctane</td>
<td>91.4 *</td>
<td>90.8</td>
<td>0.6</td>
<td>1,6-Oxido[10] annulene (17)</td>
<td>108.0 ± 0.5 *</td>
<td>69.1</td>
<td>38.9</td>
</tr>
<tr>
<td>Cyclooctene</td>
<td>80.5 ± 0.6 *</td>
<td>81.0</td>
<td>-0.5</td>
<td>trans-15,16-Dimethyl-15,16-</td>
<td>210 ± 15 *</td>
<td>129</td>
<td>81</td>
</tr>
<tr>
<td>1,3-Cyclooctadiene</td>
<td>72.8 ± 0.8 *</td>
<td>72.0</td>
<td>0.8</td>
<td>dihydride (18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,5-Cyclooctadiene</td>
<td>71.5 ± 0.7 *</td>
<td>71.2</td>
<td>0.3</td>
<td>1,3,6,8,15,16-Hexamethyl-15,16-</td>
<td></td>
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</tr>
<tr>
<td>1,3,5-Cyclooctatriene</td>
<td>-65.1 ± 0.8 *</td>
<td>64.0</td>
<td>4.3</td>
<td>dihydride (19)</td>
<td></td>
<td></td>
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<tr>
<td>Cyclooctatetraene</td>
<td>53.9 *</td>
<td>54.8</td>
<td>-0.9</td>
<td>Acepleadiene (20)</td>
<td>155 ± 5 *</td>
<td>98</td>
<td>53</td>
</tr>
<tr>
<td>Cyclooctadecanmide</td>
<td>127 ± 1 *</td>
<td>126.4</td>
<td>0.6</td>
<td>Dicyclopenta [e,f,k] heptalene</td>
<td>151 ± 4 *</td>
<td>98</td>
<td>53</td>
</tr>
<tr>
<td><strong>Benzenoid Aromatic Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td>Acenaphthylene (22)</td>
<td>111.6 *</td>
<td>72.3</td>
<td>39.3</td>
</tr>
<tr>
<td>Benzene</td>
<td>54.8 *</td>
<td>41.1</td>
<td>13.7</td>
<td>Acenaphthene (23)</td>
<td>109.3 *</td>
<td>82.4</td>
<td>26.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>66.1 *</td>
<td>53.3</td>
<td>12.8</td>
<td>Acepleadiene (24)</td>
<td>135 ± 3 *</td>
<td>106</td>
<td>29</td>
</tr>
<tr>
<td>Styrene</td>
<td>68.2 *</td>
<td>55.6</td>
<td>12.6</td>
<td>2-Phenyl-5,7-dimethyl-</td>
<td></td>
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<tr>
<td>Indene</td>
<td>80.5 ± *</td>
<td>61.4</td>
<td>19.1</td>
<td>p-isopropenyltetralene (28)</td>
<td>179 ± 4 *</td>
<td>149</td>
<td>30</td>
</tr>
<tr>
<td>Fluorene</td>
<td>110.5 *</td>
<td>84.8</td>
<td>24.7</td>
<td>3,5-Dimethylacroleinheptalene (26)</td>
<td>112 ± 3 *</td>
<td>112</td>
<td>0.0</td>
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<tr>
<td>Triphenylmethane</td>
<td>166 *</td>
<td>125</td>
<td>42</td>
<td>Pentafulvone (27)</td>
<td>43 *</td>
<td>41.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Stilbene</td>
<td>120 *</td>
<td>82</td>
<td>28</td>
<td>54.8</td>
<td>41.9</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>1,4-Diphenylbutadiene</td>
<td>130 ± *</td>
<td>105</td>
<td>24</td>
<td>94 ± 3 *</td>
<td>94.8</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>103.3 *</td>
<td>77.1</td>
<td>26.2</td>
<td>Heptalene (30)</td>
<td>72 ± 7 *</td>
<td>78.2</td>
<td>-6</td>
</tr>
<tr>
<td>1,5-Diphenylbenzene</td>
<td>152 *</td>
<td>113</td>
<td>39</td>
<td>Heptalifenalene (31)</td>
<td>94 ± 3 *</td>
<td>92.0</td>
<td>2</td>
</tr>
<tr>
<td>Biphenylene (3)</td>
<td>88 ± 3 *</td>
<td>74</td>
<td>14</td>
<td>9,10-Dimethylbenzobiphenylene (32)</td>
<td>132 *</td>
<td>146 *</td>
<td>-14</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>91.9 *</td>
<td>61.4</td>
<td>30.5</td>
<td>7,7-Dimethylbenzoquinovulene</td>
<td>105 *</td>
<td>103 *</td>
<td>2</td>
</tr>
<tr>
<td>Anthracene</td>
<td>130.3 *</td>
<td>81.7</td>
<td>48.6</td>
<td>7-Phenylbenzoquinovulene</td>
<td>131 *</td>
<td>130 *</td>
<td>1</td>
</tr>
</tbody>
</table>


Criteria of aromaticity. Magnetic criteria.

Hyp J. Daubén, Jr., James D. Wilson, and John L. Laity JACS, 1969, 91, 1991
Criteria of aromaticity. Magnetic criteria.

C. NMR Chemical Shifts

Later. Low temp? 0.61, 7.9ppm

5.58ppm

Fig. 2.—N.m.r. spectrum of [14]annulene (I) (60 Mc./sec.; deuteriochloroform solution).


F. Sondheimer et. al. *JACS*, 1962, 84, 4307
Criteria of aromaticity. Magnetic criteria.

C. NMR Chemical Shifts

Fig. 4.—N.m.r. spectrum of [18]annulene (V) (60 Mc./sec.; perdeuterio-tetrahydrofuran solution).

Area ratio 2:1

Fig. 5.—N.m.r. spectrum of tridehydro-[18]annulene (VI) [60 Mc./sec. (Varian A60 spectrometer); deuteriochloroform solution].

F. Sondheimer et. al. JACS, 1962. 84, 4307
Criteria of aromaticity. Magnetic criteria.

C. NMR Chemical Shifts

Later.
12; 5 ppm

Fig. 6.—N.m.r. spectrum of [24]annulene (e.g., VIII) (50.4 Mc./sec.; deuteriochloroform solution).

F. Sondheimer et. al. JACS, 1962, 84, 4307; ibid, 1973, 95, 7337
Criteria of aromaticity. Magnetic criteria.

C. NMR Chemical Shifts

\[ \begin{align*}
\text{n=7~} & \delta = -5.64 \\
\text{n=8~} & \delta = -4.28 \\
\text{n=9~} & \delta = -1.46 \\
\text{n=10~} & \delta = +0.07
\end{align*} \]

Figure 1. Plot of NICSs (ppm) vs the aromatic stabilization energies (ASEs, kcal/mol) for a set of five-membered ring heterocycles, C\textsubscript{4}H\textsubscript{4}X (X = as shown) (cc = 0.966).

T. S. Sorensen* and S. M. Whitworth JACS, 1990, 112, 8135
Paul von Rague Schleyer et.al. JACS, 1996, 118, 6317
Aromaticity. Annulenes.

\[
\begin{align*}
\text{144°} & \\
\end{align*}
\]

\[
\begin{align*}
\text{1. Br}_2 & \quad \Rightarrow \quad \text{2. KOH} \\
\end{align*}
\]

\[
\begin{align*}
6.8-7.5 \text{ ppm, A}_2\text{B}_2\text{-system, 8H} & \\
-0.5 \text{ ppm, s, 2H} & \\
\text{XRay: 1.37-1.42 Å, nonplanar} & \\
\end{align*}
\]


Aromaticity. Annulenes.

Low temp. H-NMR:

<table>
<thead>
<tr>
<th>n</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>22</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner</td>
<td>5.7-5.8</td>
<td>8</td>
<td>-0.61</td>
<td>10.56</td>
<td>-2.99</td>
<td>-0.4-1.2</td>
<td>11.2-12.9</td>
</tr>
<tr>
<td>Outer</td>
<td>5.7-5.8</td>
<td>6</td>
<td>7.88</td>
<td>5.33</td>
<td>9.28</td>
<td>8.5-9.6</td>
<td>4.7</td>
</tr>
<tr>
<td>Planarity (X-RAY)</td>
<td>not</td>
<td>fig</td>
<td>fig</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[20]- and [30]-annulenes were not homogenous

Aromaticity. Dehydroannulenes.

<table>
<thead>
<tr>
<th>H-NMR of dehydroannulenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
</tr>
<tr>
<td>-tropic</td>
</tr>
</tbody>
</table>

[28]-dehydroannulene has too low solubility

[18]-annulene –NO₂, MeCO, Br, CHO
[14]- and [12]-bisdihydroannulenes were electrophilically substituted

Aromaticity. Kekulene.

H.A. Staab et al. Chem. Ber., 1983, 116, 3504; ibid, 3487
Aromaticity. Cyclophanes

Benzene \( HSE_{\text{calc}} = -28.1 \text{kcal/mol} \)

\( n = 5 \quad \varphi = 23.7 \quad HSE_{\text{calc}} = +50.1 \text{kcal/mol} \)

\( n = 6 \quad \varphi = 18.6 \quad HSE_{\text{calc}} = +26.3 \text{kcal/mol} \)

\( n = 7 \quad \varphi = 14.2 \quad HSE_{\text{calc}} = +12.9 \text{kcal/mol} \)

\( n = 8 \quad \varphi = 8.4 \quad HSE_{\text{calc}} = +6.3 \text{kcal/mol} \)

Benzene 160° = -13.1 kcal/mol

Energetic no?
Structural (planar) no
Structural (bond alt) yes
NMR yes

\( \delta = 0.01 \text{ppm} \)

\( \delta = 0.22 \text{ppm} \)

\( 2.1/2.8 \text{ppm} \)

Figure 3. The theoretical molecular structure of [5]paracyclophane based on the double-\( \zeta \) (DZ) self-consistent-field (SCF) method. This sketch shows only the geometrical parameters for the benzene ring portion of the molecule. Refer to the supplementary material (Table Ia) for a complete set of geometrical parameters. In parentheses is given the minimum basis set structure of ref 25.

H.F. Schaefer III et al. JACS, 1987, 109, 2902

Friedrich Bickelhaupt et al. JACS, 1985, 107, 3716
Aromaticity. Aromatic ions.

$pK_R^+$'s of Some Cyclopropenyl Cations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium $^a$</th>
<th>Method $^b$</th>
<th>$pK_R^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipropylcyclopropenyl perchlorate (IIa)</td>
<td>A</td>
<td>a</td>
<td>2.7</td>
</tr>
<tr>
<td>Tripropylcyclopropenyl perchlorate (V)</td>
<td>A</td>
<td>a</td>
<td>7.2</td>
</tr>
<tr>
<td>Trianisylcyclopropenyl bromide $^3$</td>
<td>A</td>
<td>a</td>
<td>6.5</td>
</tr>
<tr>
<td>Dianisylphenylcyclopropenyl bromide $^3$</td>
<td>B</td>
<td>b</td>
<td>6.4</td>
</tr>
<tr>
<td>Triphenylcyclopropenyl bromide $^3$</td>
<td>B</td>
<td>b</td>
<td>5.2</td>
</tr>
<tr>
<td>Diphenylcyclopropenyl bromide $^4$</td>
<td>B</td>
<td>b</td>
<td>3.1</td>
</tr>
<tr>
<td>Propyldiphenylcyclopropenyl fluoroborate (VII)</td>
<td>B</td>
<td>b</td>
<td>-0.67</td>
</tr>
</tbody>
</table>

$^a$ A, 50% aqueous acetonitrile; B, 23% aqueous ethanol
$^b$ a, potentiometric titration; b, spectrophotometric titration.

Breslow, R. et al. JACS, 1962, 84, 3168;
Aromaticity. Aromatic ions.

\[ \text{pK}_a = 10^{-39} \quad \text{pK}_a = 10^{-16} \]

Bates, R.B. et.al. JACS, 1977, 99, 6126;
Breslow, R. et.al. JACS, 1962, 84, 3168;
Aromaticity. Aromatic ions.

\[
\text{Sbf}_5/\text{SO}_2 \rightarrow 2^+ \quad \text{[C}_8\text{H}_4\text{]}_2^2- \quad \text{[K(ClO}_3\text{CH}_3\text{CH}_2\text{O})_2]\text{[C}_8\text{H}_4\text{]}\text{[CH}_3\text{]}_4
\]

\[\delta H = 3.68 \text{ppm} \quad \delta C_{\text{ring}} = -14(\text{CS}_2) \quad \delta \text{CS}_2 = 190 \text{ppm} \quad \delta H = 5.78 \text{ppm}\]

T.J.Katz. *JACS*, 1960, 82, 3784, 3385
K.N.Raymond et.al. *JACS*, 1974, 96, 1348
Aromaticity. Aromatic ions.

R=Me; $H_{Me}$ from -4.25 to 21ppm
$H_{out}$ 8-8.7 to -3-4ppm

7:3 ratio 29.5, 28.1ppm -1.1ppm

Stable 100°C 2days

8.3, 7.4ppm vs. 5.33

H-NMR spectra similar

Antiaromaticity

**Kinetic acidity study**

\[ \psi_2 \]

\[ \psi_1 \]

**Thermodinamic acidity study**

\[ R - H \rightleftharpoons R - OH \rightleftharpoons R^+ \rightarrow e^- \rightarrow R^- \rightarrow K_{eq} \rightarrow R - H \]

\[ pK_a \geq 51 \]

\[ pK_a = 31 \]

Figure 1. (a) Na₂Fe (CO)₄; (b) K₂CO₃/D₂O; (c) CH₃CO₂N—N—CO₂CH₃/∆; (d) N-bromosuccinimide; (e) 2,6-lutidine; (f) KOBu+/Me₂SO; (g) Pb(OAc)₄.

B.K.Carpenter JACS, 1980, 102, 4272
Figure 1. Methyl tri-tert-butyl[4]annulencarboxylate. Selected bond distances and angles are given and the estimated standard deviations of the bond distances and angles are 0.005 Å and 0.3°, respectively. The three sites (occupancies 0.51, 0.32, 0.17) of the disordered methyl groups bonded to C15 are designated as 1, 2, and 3, respectively.

S. Masamune et. al JACS, 1975, 97, 1973
S. Masamune et. al JACS, 1973, 95, 8481
Figure 1. Nmr spectral data for the (potassium) benzocycloheptatrienyl anion (2) in ammonia-d₈ at -50° (with trimethylamine (δTMS 2.135) as internal standard) and the benzocycloheptatrienyl cation¹³ (4) in acetonitrile-d₈ at 32° (with TMS as internal standard).¹⁸a

Staley, S.W. JACS, 1973, 95, 3382
Homoaromaticity

Buchner acid

Winstein, S. JACS, 1959, 81, 6524
Applequist, D.E.; Roberts, J.D. JACS, 1956, 78, 4012
Doering W.v.E. et al. JACS, 1956, 78, 5448
Homoaromaticity

35 $X = \text{NH}$
36 $X = \text{O}$
37 $X = \text{BH}$

$\Delta E = 8.8 \text{kcal/mol}$

More stable

$\Delta E = 47 \text{kcal/mol}$

<table>
<thead>
<tr>
<th>#</th>
<th>35</th>
<th>36</th>
<th>37</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5(A)</td>
<td>1.74</td>
<td>1.71</td>
<td>2.00</td>
<td>1.65</td>
</tr>
</tbody>
</table>

1.400$\pm$0.004A
1.7$\pm$2.0A
$\Delta E = 22.3 \text{kcal/mol}$
2-6: 8.6ppm
1,7: 6.6ppm


R. Petit et al. *JACS*, **1962**, 84, 2842
Homoaromaticity. Hydroxy-homotropylum cation.

Figure 2. The cation C₆H₅(OH)⁺ showing the atom numbering.

Figure 3. The cation C₆H₅(OH)⁺ showing the dihedral angles between planes of atoms (temperature factors are isotropic for simplicity).

Table IV. Selected Interatomic Distances (Å) and Angles (Deg)

<table>
<thead>
<tr>
<th>Interatomic Distances</th>
<th>Possible Hydrogen Bonds</th>
<th>Interatomic Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(1)–Cl(11)</td>
<td>2.363 (2)</td>
<td>O(2)⋯Cl(11)</td>
</tr>
<tr>
<td>Sb(2)–Cl(22)</td>
<td>2.365 (1)</td>
<td>O(2)⋯Cl(12)</td>
</tr>
<tr>
<td>C(3)–C(4)</td>
<td>1.378 (13)</td>
<td></td>
</tr>
<tr>
<td>C(2)–O(2)</td>
<td>1.182 (12)</td>
<td></td>
</tr>
<tr>
<td>O(2)⋯Cl(22)a</td>
<td>3.292 (9)</td>
<td></td>
</tr>
<tr>
<td>Cl(11)–Sb(1)–Cl(12)</td>
<td>90.4 (1)</td>
<td>Cl(11)–Sb(1)–Cl(12)a</td>
</tr>
<tr>
<td>C(12)–Sb(1)–Cl(12)c</td>
<td>89.6 (1)</td>
<td>Cl(21)–Sb(2)–Cl(22)</td>
</tr>
<tr>
<td>Cl(22)–Sb(2)–Cl(22)d</td>
<td>90.1 (1)</td>
<td>Cl(22)–Sb(2)–Cl(22)e</td>
</tr>
<tr>
<td>C(1)–C(2)–C(3)</td>
<td>128.9 (7)</td>
<td>C(2)–C(3)–C(4)</td>
</tr>
<tr>
<td>C(7)–C(1)–C(2)</td>
<td>127.0 (7)</td>
<td>C(8)–C(1)–C(7)</td>
</tr>
<tr>
<td>C(1)–C(2)–O(2)</td>
<td>115 (1)</td>
<td>C(3)–C(2)–O(2)</td>
</tr>
</tbody>
</table>

\[a\] Atoms are related to those given in Table II: \(a, -x, y, -z; b, x, -y, z; c, -x, -y, -z; d, 1-x, y, -z; e, 1-x, 1-y, -z; f, x, 1-y, z.\)

R.F. Childs et al. *JACS, 1982, 104, 2452*
Homoaromaticity. Neutral molecules.

Conclusions

• Definition of Aromaticity is not a simple matter
• Ring current is the major used manifestation of Aromaticity
• If a structure can be planar, it will be aromatic (4n+2 annulenes, n<6-8)
• If a structure can (or forced) to be planar, it can be antiaromatic (4n annulenes, n<6-8)
• Both are quantitative and it is proper to talk about degree of (anti-)aromaticity, rather than if it is aromatic or not
Appendix A: Structures of certain aromatic / pseudoaromatic compounds

Figure 1. Structures of certain aromatic and pseudoaromatic compounds.


Landineer et al. TL, 1975, 349
Appendix C. Cyclodecapentacene

E.E. van Tamelen and T.L. Burloth *JACS*, 1967, 89, 151
[14]-annulene X-RAY study

Stereoscopic view of a molecule of [14]annulene. The thermal ellipsoids are scaled to 25% probat

Planarity: +/-0.21Å (C)  
 +/-0.79Å (H)

Bonds vary,  
No real alteration

Figure 2. Molecular dimensions in [14]annulene. The upper half of the drawing shows the bond lengths (angströms) and bond angles (degrees). The lower part of the drawing (related by a center of inversion) shows the deviations of atoms (angströms) from the best plane through the carbon atoms, and the torsion angles around the C-C bonds (degrees). The esd's of the C-C bonds are 0.010 Å and of the C-C-C angles are 0.5°. According to the formula given by P. J. Huber in the appendix in E. Huber-Buser and J. D. Dunitz, Helv. Chim. Acta, 44, 2027 (1961), the esd's of the torsion angles are approximately twice those of the valency angles.

Chian C. Chiang, Iain C. Paul
W. A. Noyes Chemical Laboratory, University of Illinois
Urbana, Illinois 61801
Received Feb 28, 1972

I.C.Paul, C.C.Chiang JACS, 1972, 94, 4741
[16]-annulene X-RAY study

Figure 1. Stereoscopic view of the [16]annulene molecule looking along the b axis. Bond distances in Ångströms; standard deviation of C–C bond distances lie in range 0.010–0.015 Å.

Figure 2. View of the [16]annulene molecule looking along the a axis. The dihedral angles along the bonds in the ring are given in degrees. The angle is taken as positive if, when viewed along the bond, the nearer substituent has to be rotated clockwise to eclipse the more distant substituent.

Average C–C=1.46Å
Average C=C=1.34Å

I.C. Paul, et al. JACS, 1968, 90, 6555